Supporting Information

Difluorobenzimidazole Decorated Helical Perylene Diimide Dimer for High-Performance N-Type Organic Field-Effect Transistor

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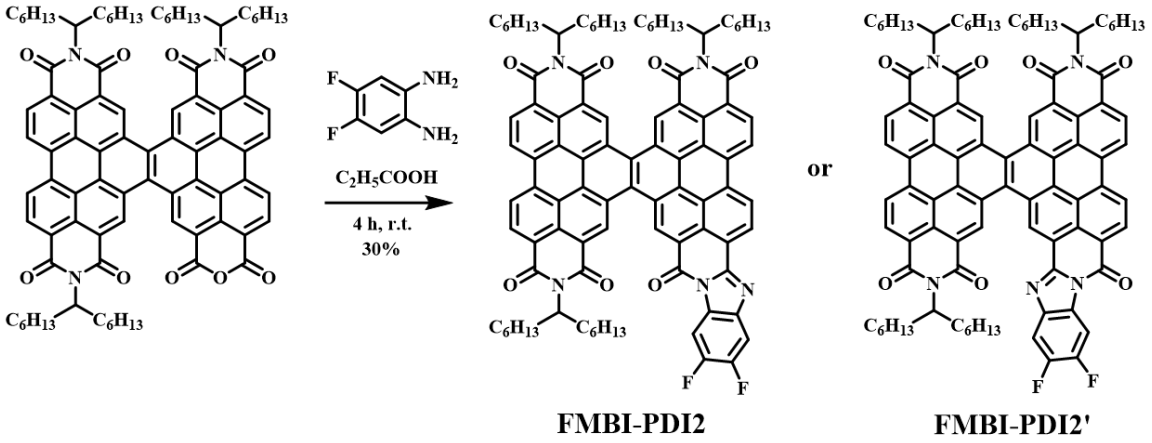
1. Material synthesis

Synthetic procedures of FMBI-PDI2. The condensation of compound **1** (300 mg, 0.224 mmol) with 4,5-difluorobenzene-1,2-diamine (162.6 mg, 1.12 mmol) in 30 mL propanoic acid at room temperature for 4 h. After adding water to the reaction mixture, precipitation was filtered. The crude products were purified by silica gel column chromatography (eluted with petroleum ether/CH_2Cl_2 = 1:4) and lead to purple solid **FMBI-PDI2** (96 mg, 30%). ^{1}H NMR (500 MHz, CF_3COOD) δ 11.09 (s, 1H,), 10.65 (d, *J* = 78.5 Hz, 3H), 10.16-9.27 (m, 8H), 9.05 (d, *J* = 22.0 Hz, 1H), 8.27-7.90 (m, 1H), 5.62 (d, *J* = 135.6 Hz, 3H), 2.54 (d, *J* = 136.2 Hz, 12H), 1.65 (d, *J* = 82.4 Hz, 48H), 1.08 (s, 16H). ^{13}C NMR (126 MHz, CF_3COOD) δ 127.56, 124.24, 32.55, 31.73, 31.65, 29.17, 28.99, 26.98, 22.44, 22.31, 18.99, 12.82, 12.66. MS (MALDI-TOF): $[M+H]^+$ calculated for 1456.714; found 1456.830.



Scheme S1 Synthetic route of **FMBI-PDI2**/**FMBI-PDI2'**

2. Thermogravimetric analysis (TGA)

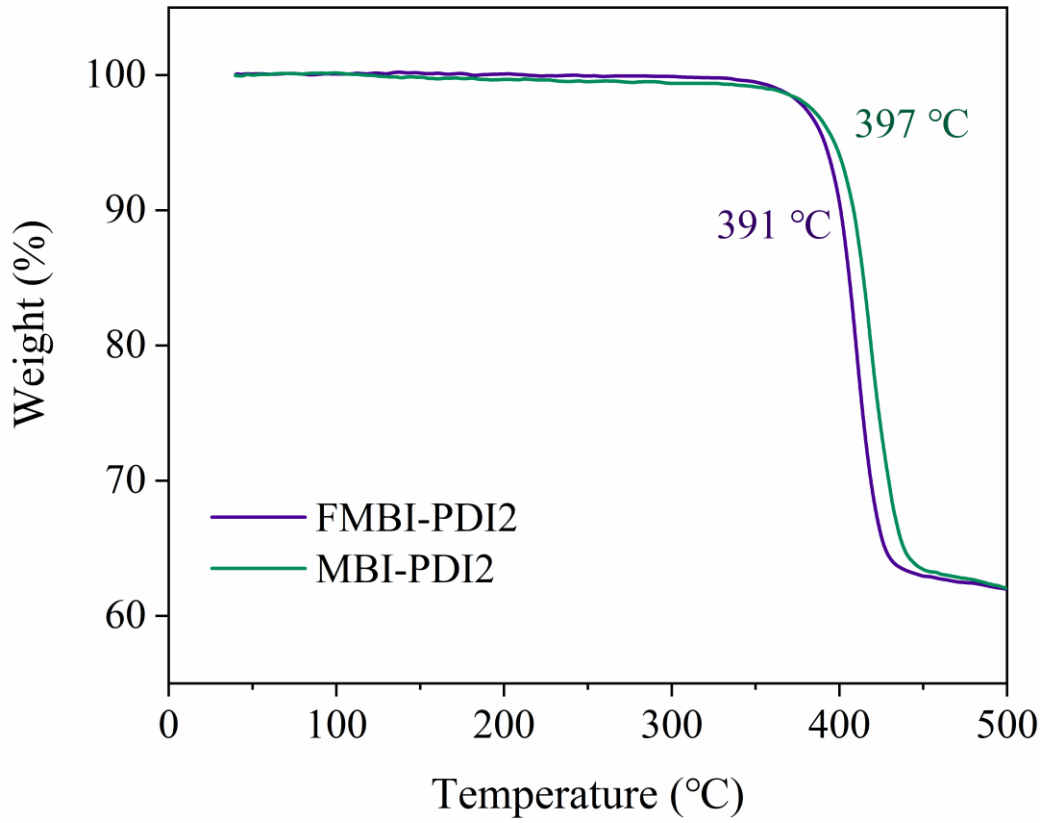


Fig. S1. TGA of **FMBI-PDI2** and **MBI-PDI2**

3. DFT calculation

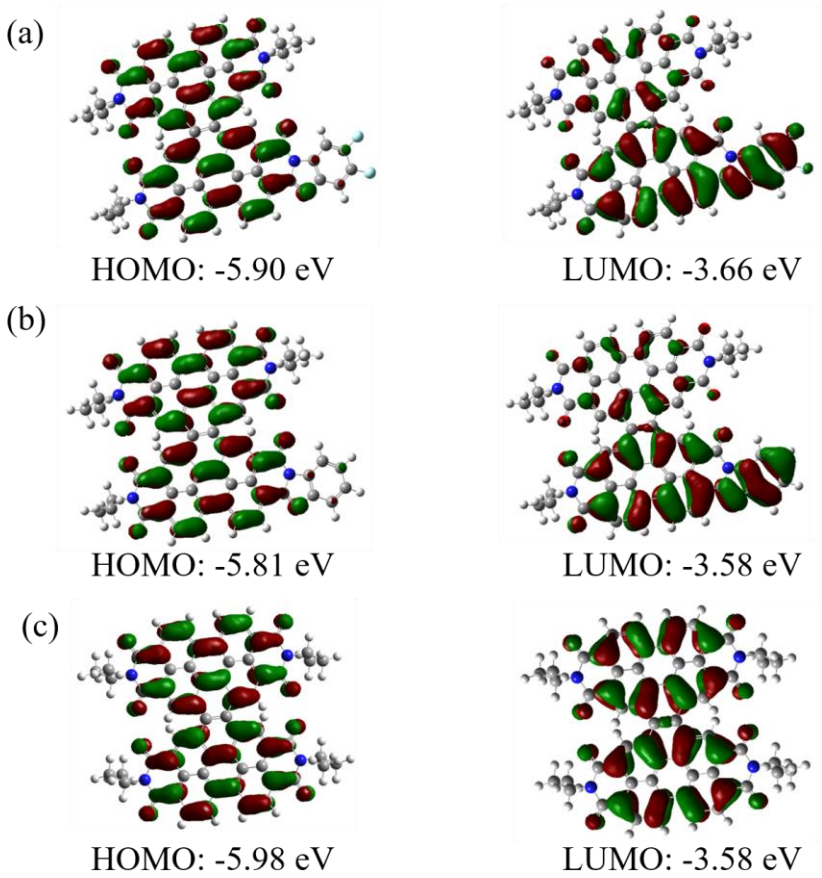


Fig. S2. Theoretical calculation of HOMO and LUMO electron density distributions of (a) **FMBI-PDI2**, (b) **MBI-PDI2** and (c) PDI2.

4. Optical and Electrochemical Properties.

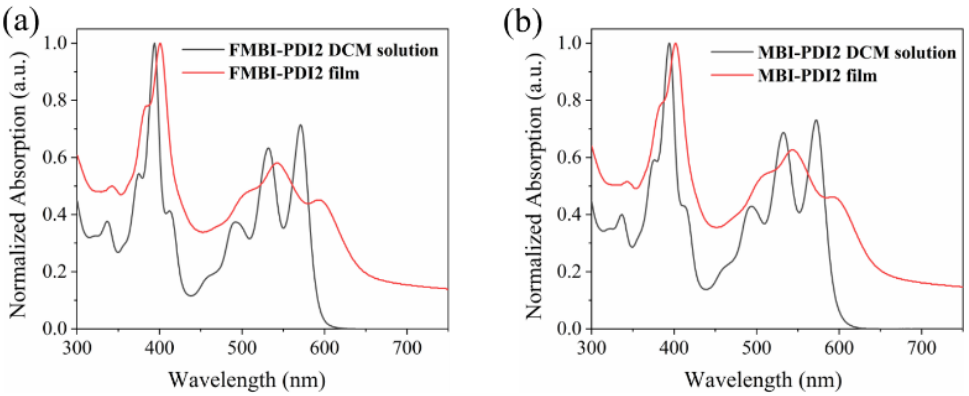


Fig. S3. The comparison profiles of absorption spectra in dichloromethane solution and films of (a) **FMBI-PDI2** and (b) **MBI-PDI2**.

5. The organic field-effect transistors (OFETs) performance of the devices

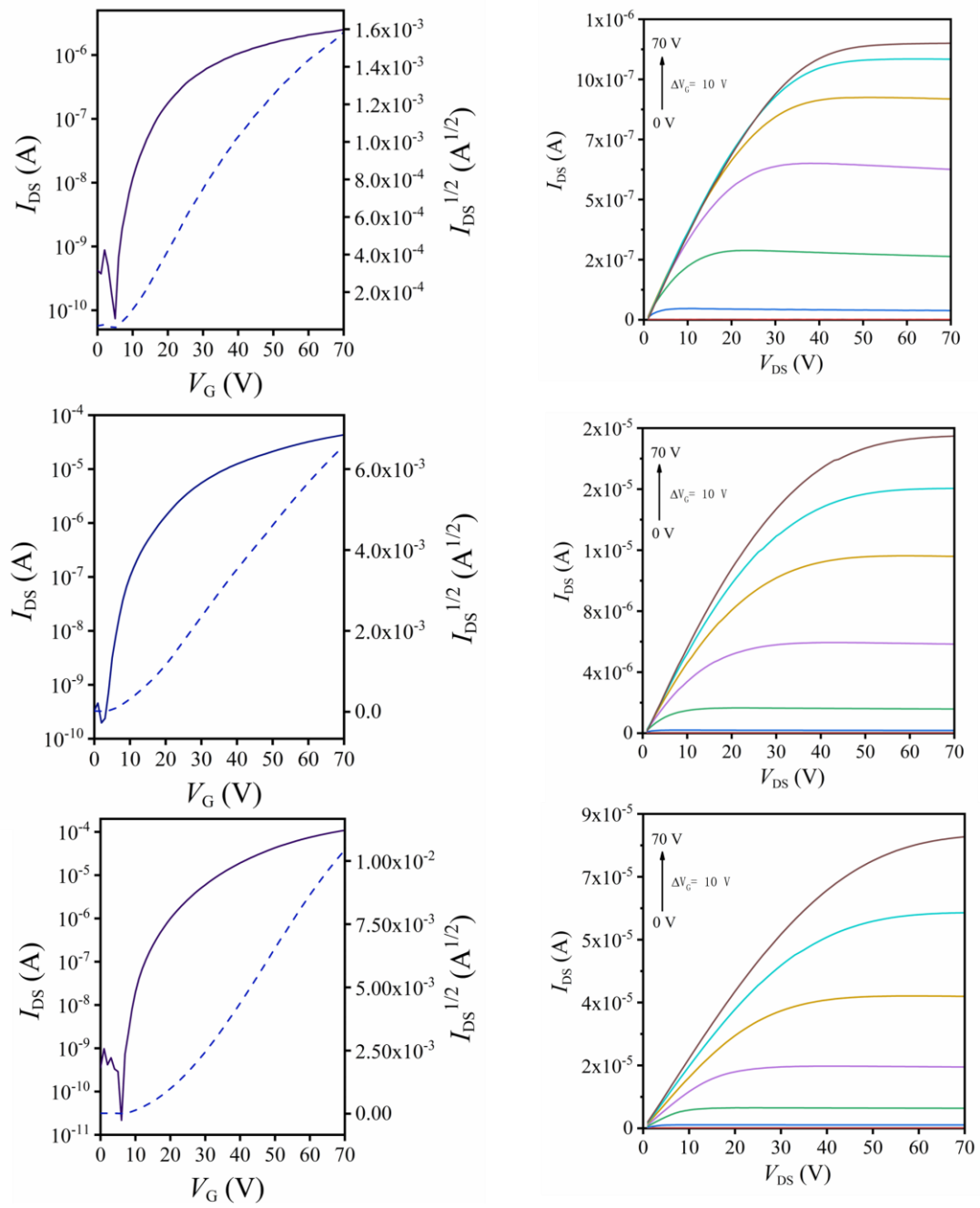


Fig. S4. Typical transfer and output characteristics of **FMBI-PDI2** based devices. Transfer and output curves (V_{DS} = 70 V) of **FMBI-PDI2** OFET devices annealed at room temperature, 180 °C, 260 °C for 10 min.

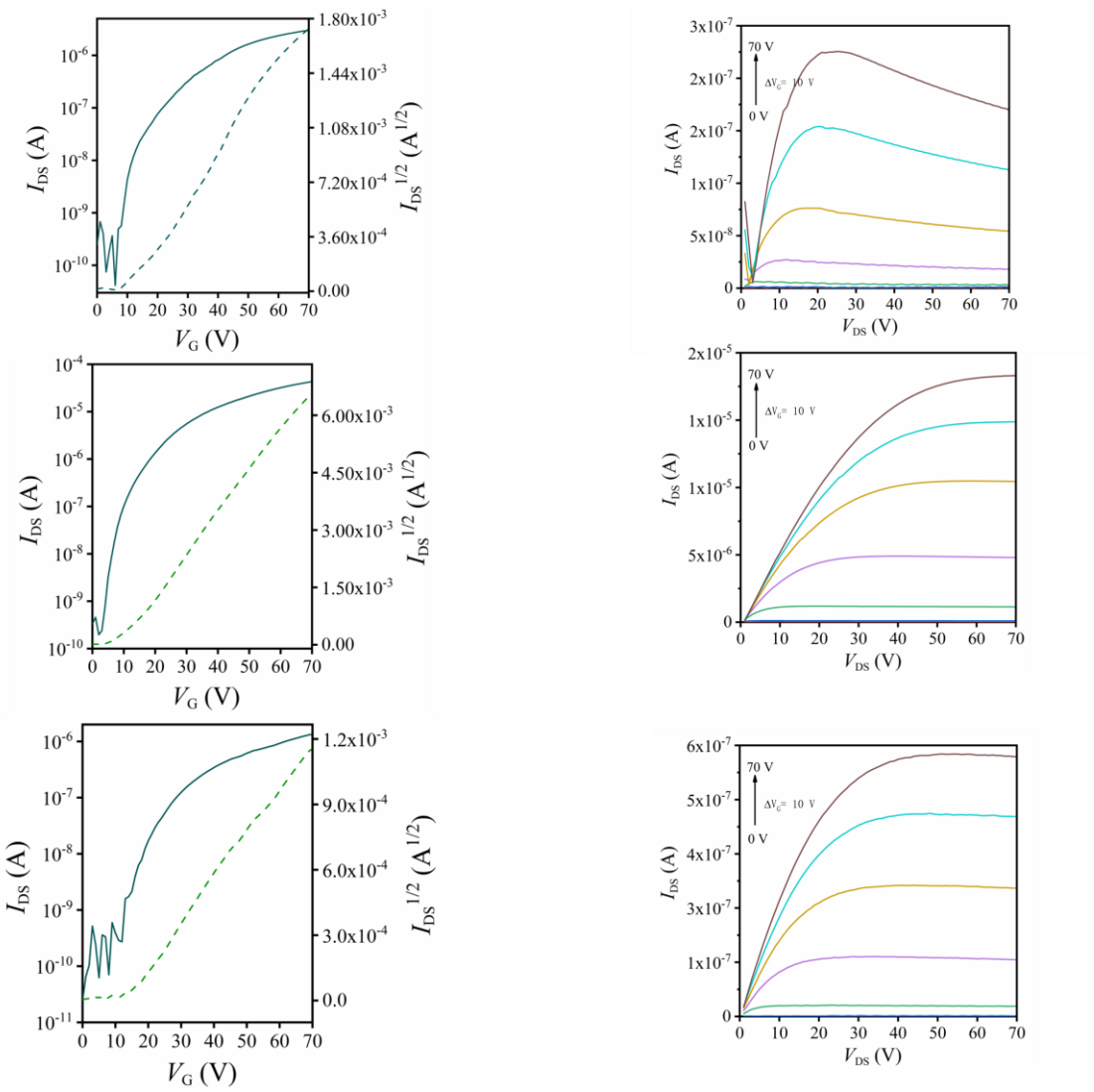


Fig. S5. Typical transfer and output characteristics of **MBI-PDI2** based devices. Transfer and output curves (V_{DS} = 70 V) of **MBI-PDI2** OFET devices annealed at room temperature, 180 °C, 260 °C for 10 min.

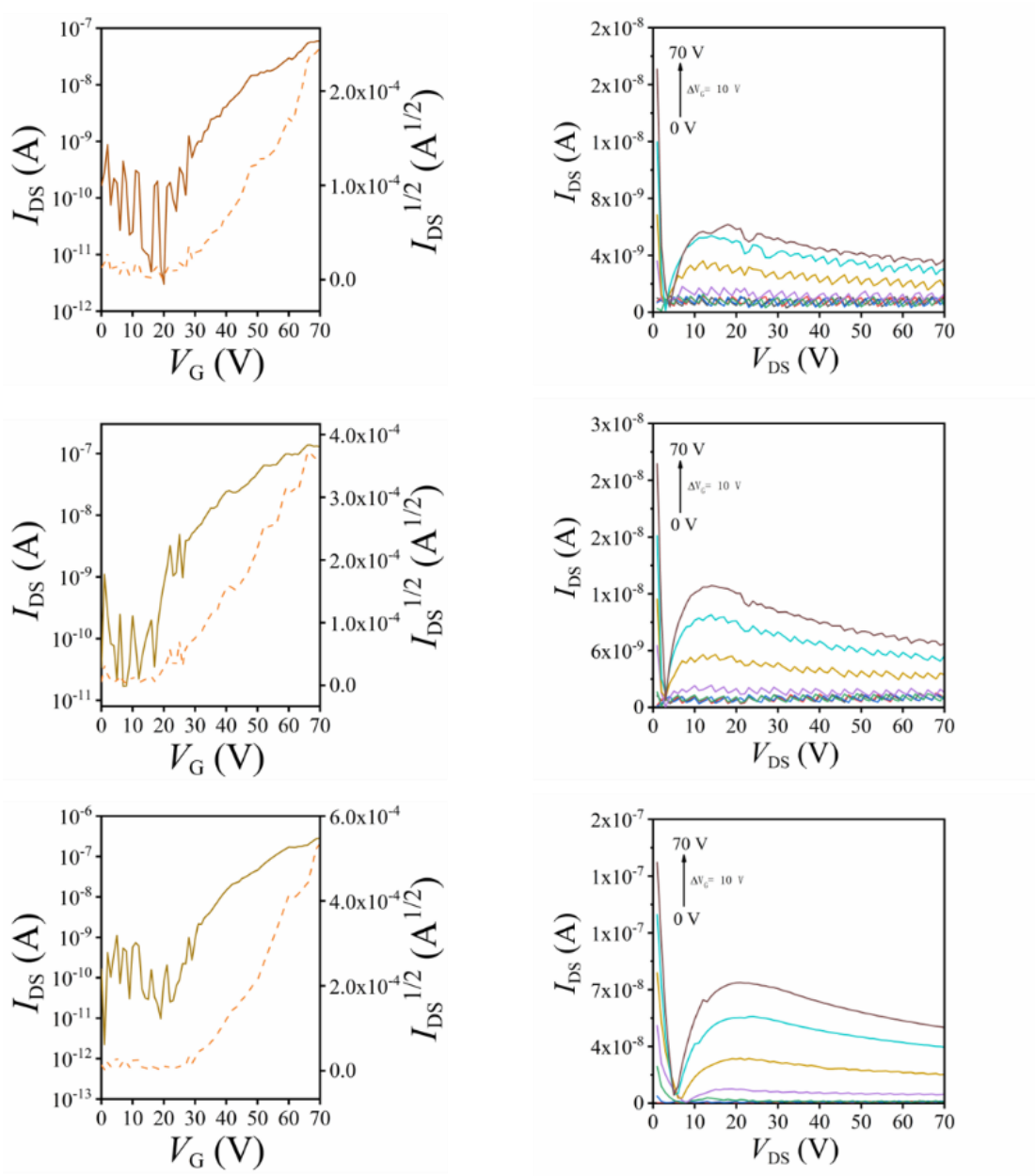


Fig. S6. Typical transfer and output characteristics of PDI2 based devices. Transfer and output curves (V_{DS} = 70 V) of PDI2 OFET devices annealed at 80 °C, 120 °C and 140 °C for 10 min.

Table S1. The thin-film transistor properties of **FMBI-PDI2**, **MBI-PDI2** and PDI2 at different annealing temperatures.

Compound	Annealing temperature (°C)	μ_e[a] ($cm^2\ V^{-1}\ s^{-1}$)	I_{ON}/I_{OFF}	V_{th} (V)
FMBI-PDI2	As cast	0.001 (0.002)	10^3	8±5
	180	0.023 (0.027)	10^5	11±3
	220	0.111 (0.131)	10^6	14±5
	260	0.081 (0.084)	10^5	19±4
MBI-PDI2	As cast	0.010 (0.012)	10^3	29±3
	180	0.025 (0.029)	10^5	28±2
	220	0.052 (0.053)	10^5	35±2
	260	0.011 (0.014)	10^4	27±2
PDI2	As cast	--	--	--
	80	7.8×10^{-5} (8.0×10^{-5})	10^3	31±2
	120	9.0×10^{-5} (1.2×10^{-4})	10^6	22±4
	140	7.2×10^{-4} (7.3×10^{-4})	10^4	32±3

[a] Average mobilities, with the maximum mobilities shown in parentheses. More than 10 devices were characterized at different annealing temperature of **FMBI-PDI2**, **MBI-PDI2** and PDI2. All devices were measured under vacuum condition.

Table S2. Summary of electronic mobility of OFET with different aromatic compounds.

Compound	**Deposition Process**	μ_e **(cm^2 V^{-1} s^{-1})**	**Ref**
Dimer 2	spin coating	0.02	
Trimer 3	spin coating	0.04	[33]
Tetramer 4	spin coating	0.05	
P1	spin coating	0.01	[65]
P1	spin coating	0.075	[66]
5a	spin coating	1.5	[67]
trans-cDBDB	spin coating	9.9×10^{-4}	[68]
FMBI-PDI2	spin coating	0.13	This work
MBI-PDI2	spin coating	0.05	This work

6. Microscopic morphology characterizations (AFM)

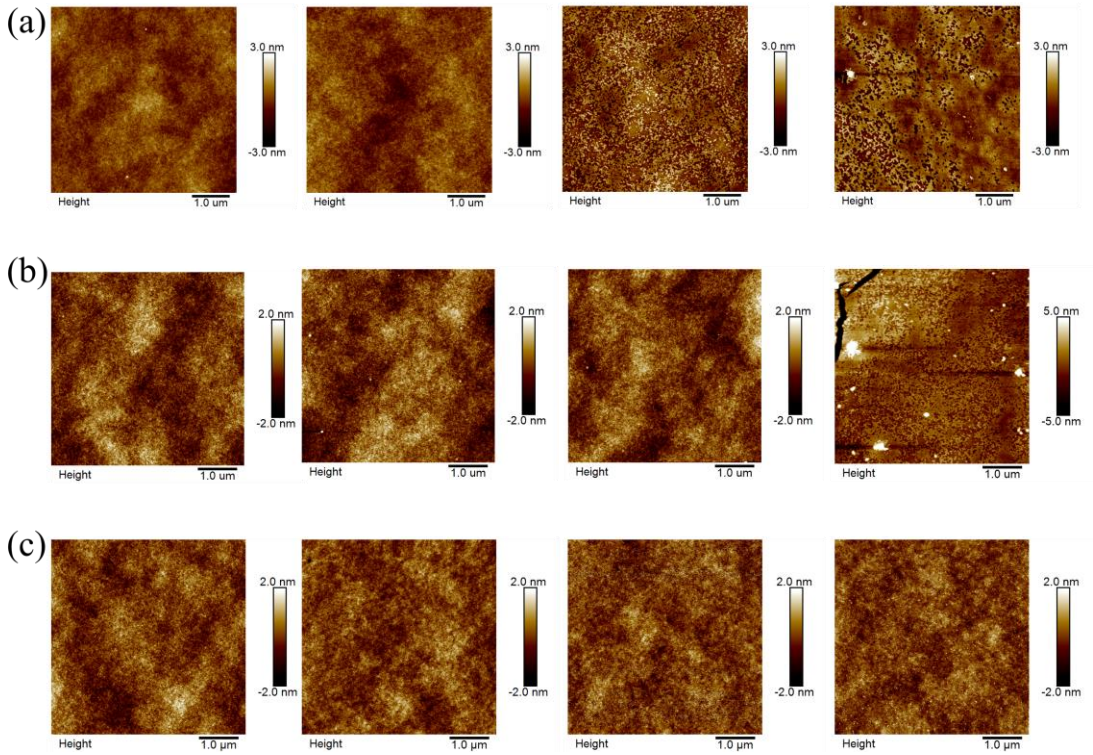


Fig. S7. AFM images of thin-films based on (a) **FMBI-PDI2**, (b) **MBI-PDI2** both at room temperature, 180, 220, 260 °C annealing temperatures and (c) PDI2 at room temperature, 80, 120, 140 °C annealing temperatures.

7. ^{1}H and ^{13}C NMR spectra

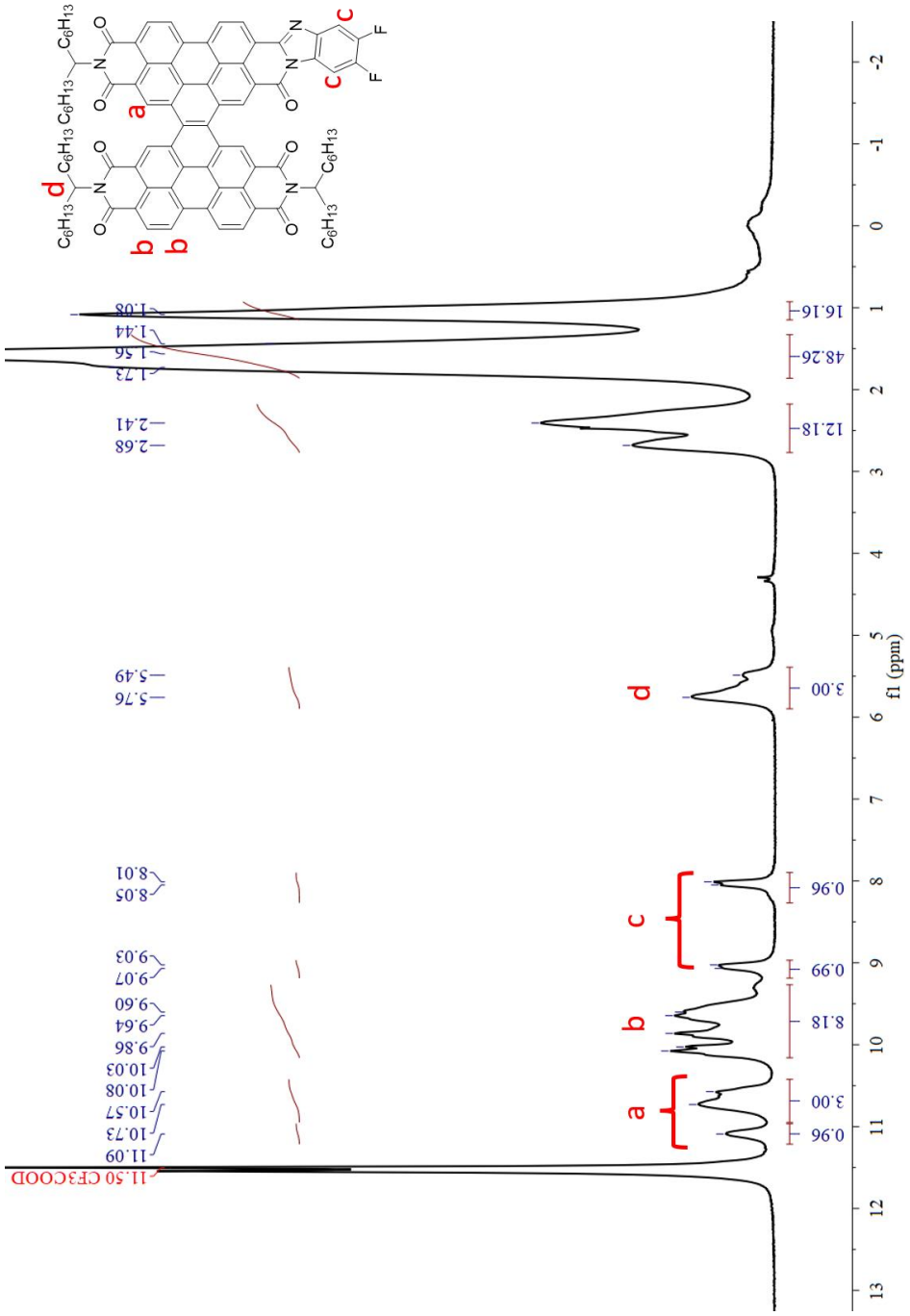


Fig. S8. ^{1}H NMR spectra of **FMBI-PDI2**.

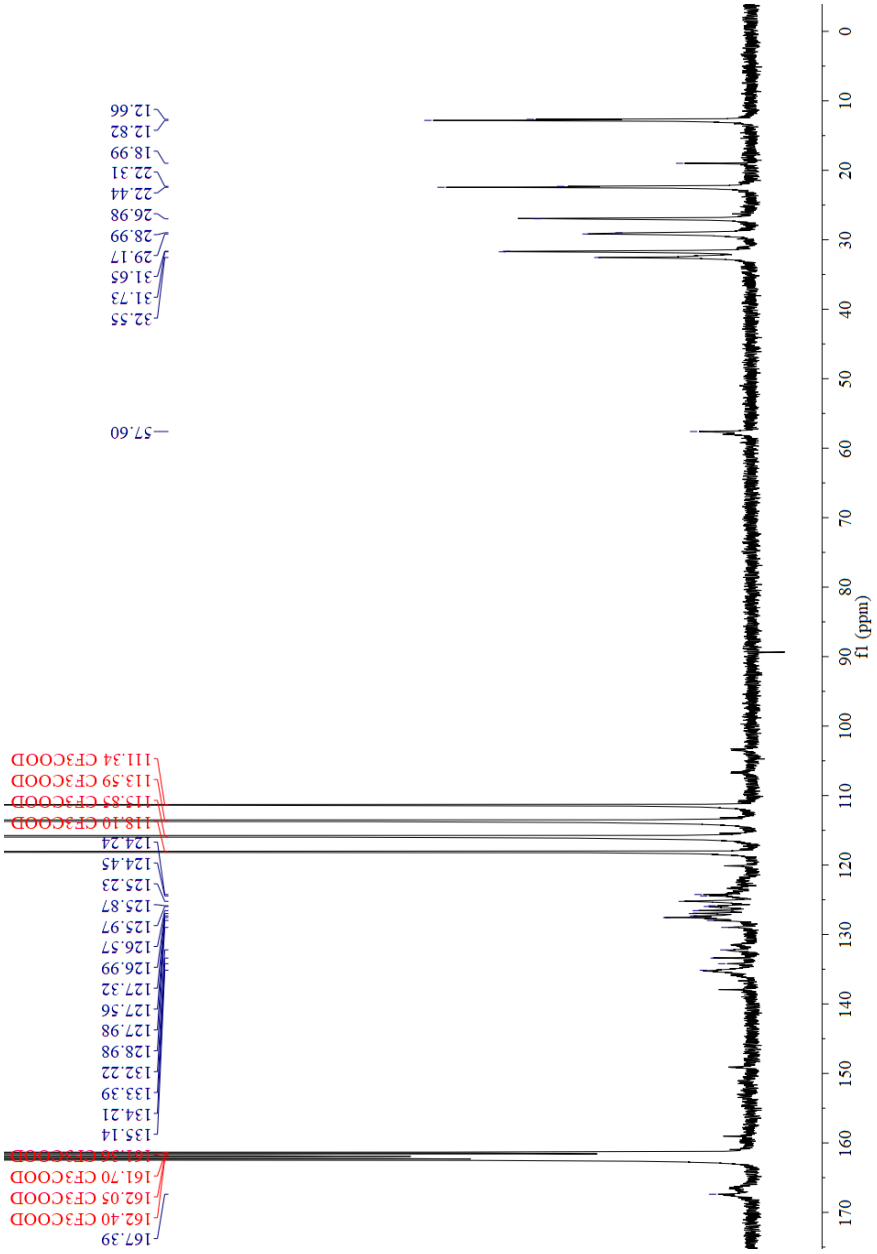


Fig. S9. ^{13}C NMR spectra of **FMBI-PDI2**.

8. MALDI-TOF Mass spectrum

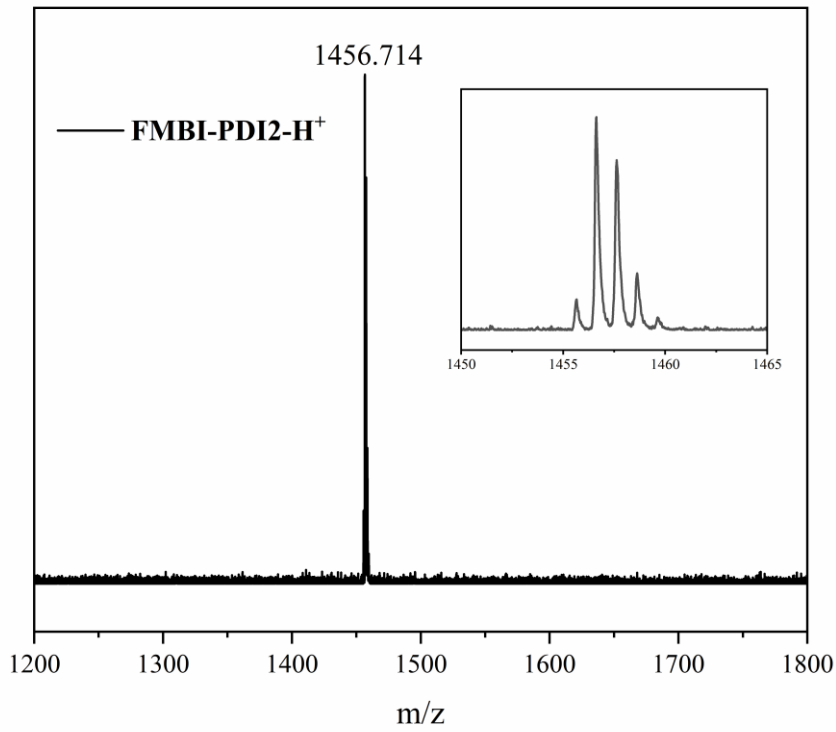


Fig. S10. MALDI-TOF mass spectroscopy of **FMBI-PDI2 with DCTB matrix** in cationic mode

9. Optimized geometry

All calculations were performed using density functional theory (DFT) with the B3LYP functional and with the 6-31G(d) basis set in the Gaussian 09 program. The energies levels of the frontier orbitals were calculated at the optimized structure.

Table S3. Standard orientation of **FMBI-PDI2**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	4.521863	-6.646587	0.268893
2	8	0	5.282939	-2.417075	-1.195043
3	6	0	6.575957	-5.878412	-1.819607
4	6	0	7.156663	-5.291616	0.609858
5	6	0	6.391605	-4.878867	-0.663006
6	7	0	-6.041279	-4.049621	0.287206
7	8	0	-4.892157	-0.088505	-0.838493
8	6	0	4.127478	-5.517458	0.073267
9	7	0	4.970679	-4.530857	-0.415233
10	6	0	4.540525	-3.240124	-0.699315
11	6	0	-4.536191	-1.179765	-0.435783
12	7	0	-5.389490	-2.103096	-0.236513
13	6	0	-5.052787	-3.268502	0.157606
14	6	0	-3.770829	-3.596164	0.384221
15	6	0	-3.392713	-4.824122	0.760667
16	6	0	-2.089062	-5.110118	0.873248
17	6	0	-2.266925	-0.495679	-0.331288
18	6	0	-3.213700	-1.435251	-0.186825
19	6	0	-2.826012	-2.656811	0.214266
20	6	0	-1.514554	-2.935409	0.365671
21	6	0	-1.121967	-4.197467	0.643004
22	6	0	0.196641	-4.501569	0.619226

23	6	0	0.654437	-5.749132	0.838132
24	6	0	1.943308	-6.072931	0.687319
25	6	0	2.832433	-5.151940	0.285525
26	6	0	1.108298	-3.552771	0.307330
27	6	0	2.404963	-3.889124	0.102647
28	6	0	3.251071	-2.952218	-0.356765
29	6	0	2.799373	-1.693646	-0.474493
30	6	0	-0.973116	-0.674499	0.004531
31	6	0	-0.600590	-1.954749	0.213515
32	6	0	0.706011	-2.268690	0.181822
33	6	0	1.586687	-1.279285	-0.062566
34	6	0	-0.074208	0.344037	0.056527
35	6	0	1.239252	0.031905	0.020803
36	8	0	-4.084721	2.822665	1.324959
37	8	0	-3.315891	7.044608	-0.154249
38	8	0	6.003249	0.410718	1.028592
39	8	0	7.148802	4.528708	-0.492237
40	6	0	-5.961038	5.722103	-0.470218
41	6	0	-5.355090	6.271910	1.961249
42	6	0	8.492853	0.831631	-0.485558
43	6	0	8.509926	1.981533	1.806685
44	6	0	8.064766	2.065090	0.335769
45	6	0	-5.188693	5.285916	0.790645
46	6	0	5.681222	1.471580	0.537259
47	7	0	6.631881	2.418736	0.187748
48	6	0	6.301828	3.690326	-0.264372
49	6	0	2.137453	1.049926	0.071145
50	6	0	3.424555	0.872139	0.422270
51	6	0	4.385401	1.794525	0.260635
52	6	0	4.030213	3.012446	-0.179250
53	6	0	4.971034	3.947445	-0.406534
54	6	0	4.568440	5.170284	-0.784263
55	6	0	3.265145	5.459052	-0.869184

56	6	0	1.781280	2.330916	-0.146837
57	6	0	2.712025	3.295065	-0.315441
58	6	0	2.305870	4.550848	-0.604850
59	6	0	-1.618666	2.078197	0.563257
60	6	0	-0.411410	1.657867	0.141795
61	6	0	0.473975	2.642762	-0.108805
62	6	0	0.075125	3.926986	-0.235149
63	6	0	0.989974	4.866195	-0.563300
64	6	0	0.535677	6.115676	-0.780604
65	6	0	-0.748433	6.449805	-0.612241
66	7	0	-3.772080	4.930258	0.529477
67	6	0	-3.345258	3.638441	0.813481
68	6	0	-2.062917	3.340281	0.453788
69	6	0	-1.216939	4.271378	-0.016608
70	6	0	-1.638575	5.536605	-0.195733
71	6	0	-2.927859	5.911834	0.033327
72	6	0	-6.660126	-2.125239	-0.360469
73	6	0	-7.053022	-3.363944	-0.025001
74	6	0	-7.595245	-1.233706	-0.727664
75	6	0	-8.892161	-1.592814	-0.753149
76	6	0	-9.265588	-2.843246	-0.412908
77	6	0	-8.337084	-3.741029	-0.044262
78	9	0	-9.807265	-0.705079	-1.117559
79	9	0	-10.542447	-3.197376	-0.438581
80	1	0	7.652855	-5.996796	-2.080583
81	1	0	6.194941	-6.895031	-1.583604
82	1	0	6.046207	-5.523526	-2.733464
83	1	0	7.003198	-4.542759	1.420967
84	1	0	6.857212	-6.284767	1.006428
85	1	0	8.252574	-5.354894	0.416521
86	1	0	6.964581	-3.979296	-1.000610
87	1	0	-4.132072	-5.626315	0.925548
88	1	0	-1.889303	-6.161440	1.124507

89	1	0	-2.580924	0.464414	-0.762715
90	1	0	0.011758	-6.595644	1.118420
91	1	0	2.219312	-7.126221	0.864130
92	1	0	3.465000	-0.959711	-0.948514
93	1	0	-5.812363	4.988598	-1.295976
94	1	0	-7.055776	5.781733	-0.269293
95	1	0	-5.665426	6.722999	-0.849845
96	1	0	-6.429342	6.402054	2.227385
97	1	0	-4.827484	5.897152	2.868428
98	1	0	-4.958985	7.285410	1.736730
99	1	0	8.131697	0.913410	-1.536702
100	1	0	9.603049	0.739085	-0.520340
101	1	0	8.122501	-0.131528	-0.074998
102	1	0	9.613745	1.851349	1.885765
103	1	0	8.241390	2.915354	2.352099
104	1	0	8.047575	1.130149	2.351115
105	1	0	8.710925	2.867360	-0.100959
106	1	0	-5.766211	4.385452	1.117909
107	1	0	3.713679	-0.085436	0.876385
108	1	0	5.277733	5.988418	-0.995677
109	1	0	3.061231	6.505376	-1.136912
110	1	0	-2.283793	1.346747	1.041653
111	1	0	1.176797	6.959521	-1.071675
112	1	0	-1.019601	7.504531	-0.788112
113	1	0	-7.349639	-0.201384	-1.014067
114	1	0	-8.624522	-4.766888	0.236492

Rotational constants (GHZ): 0.0319547 0.0196837 0.0124691

nuclear repulsion energy 12760.6886065306 Hartrees.